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On explosive reactions of gases II : spark ignition of oxyhydrogen gas at low pressures

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ON EXPLOSIVE REACTIONS OF GASES.

II. Spark Ignition of Oxyhydrogen Gas at Low Pressures.

By AKIO HAYAKAWA and REMPEI GOTO.

Introduction.

The upper pressure limit in the case of the thermal explosion of a combustible gas mixture at low pressures has been considered to be determined mainly by the condition of the gaseous phase, and to be independent of the surface of the vessel used¹⁾. In the experimental proof of it, Lavrov²⁾ adduced the fact that the upper pressure limit is found also at an explosion induced by electric spark discharge. Fig. 1 shows the result which Lavrov obtained and has been regarded to support the chain theory of explosion developed by Semenov³⁾. Thompson⁴⁾ found, by observing the lower pressure limit of spark ignition of oxyhydrogen gas, the chain theory applicable to his own result. Both Lavrov and Thompson, however, have made no radical consideration on the spark ignition.

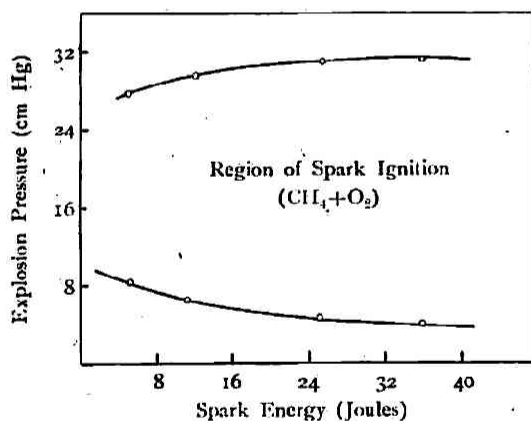


Fig. 1.

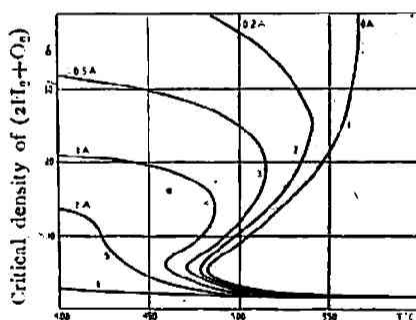


Fig. 2. Critical density of an igniting mixture of 2H₂+O₂. (1) Region of inflammation, (2), (3), (4), (5), (6), regions of inflammation for different spark energies. (Gorchakov.)

Gorchakov's result⁵⁾ cited by Semenov shows the fact that the upper limit rises according as spark energy increases; i.e. the explosion region is extended and the upper limit finally disappears, leaving only the lower limit (Fig. 2). Though

- 1) C. N. Hinshelwood and A. T. Williamson, *The Reaction between Hydrogen and Oxygen*. Oxford (1934).
- 2) Lavrov and Bestchastny, *Acta Physicochim.*, 1, 975 (1934).
- 3) Semenov, *Chemical Kinetics and Chain Reactions*, Oxford. (1935).
- 4) Thompson, *Trans. Faraday Soc.*, 28, 299 (1932).
- 5) Semenov, *loc. cit.*, p. 212.

no explanation has been given to the result, this fact is considered to show that the upper limit is determined not by the conditions of the gaseous phase, but by the other condition, that is, the kind and degree of the energy externally applied. Besides, it cannot be affirmed that the spark discharge exerts no influence on the state of the surface of the vessel used, because the emission of the spark not only gives thermal, electric, and photo-chemical effects to gaseous molecules, but is also accompanied by remarkably strong pressure waves or sound waves.

Concerning spark discharge in a gas, the following experimental law has been established:—

"At a given temperature, the sparking potential (V_s) in uniform electric field is the function of the product of spark gap (d mm) and gas pressure (P mm Hg):"

This law was found experimentally by Paschen in 1889, being applicable to most gases except the case of higher pressures. As to the air, for instance, the result shown in Fig. 2 has been obtained⁶⁾. Though the present authors do not know any instance which confirms the application of Paschen's Law to such a chemically reactive gas mixture as oxyhydrogen gas there may be found a relation qualitatively analogous to that shown Fig. 3.

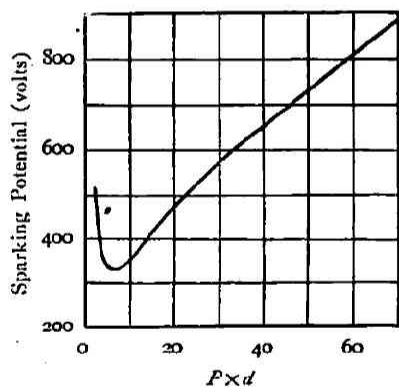


Fig. 3.

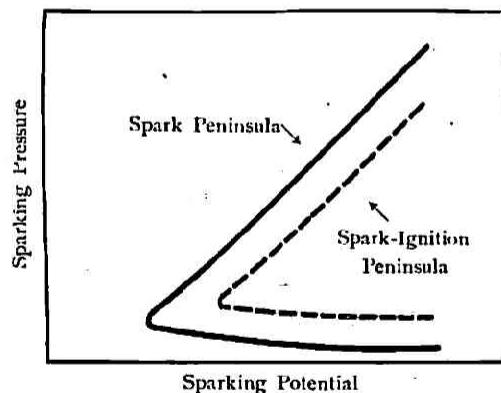


Fig. 4.

As spark energy is the function of the sparking potential V_s , if there is such a relation as given in Fig. 1, the explosion pressure P is to be expressed as the function of V_s . If there is no emission of spark, no explosion can occur. Therefore, the region of spark ignition must be included in the sparking region, and the relation between the sparking region and the region of sparking ignition at a constant spark gas is to be schematically drawn as in Fig. 4. This is another expression for Fig. 3 and Fig. 1. Let us name these two sorts of curves 'spark

6) L. B. Loeb, *Fundamental Process of Electrical Discharge in Gases*, p. 411, New York (1939).

peninsula' and 'spark ignition peninsula' respectively. These curves correspond to the thermal explosion peninsula in type, though the experimental conditions are different.

The aim of the present paper is to confirm 'spark peninsula' and 'spark ignition peninsula' with regard to oxyhydrogen gas with reference to spark ignition and thermal explosion.

Apparatus.

The electric connection for the emission of spark is shown in Fig. 5. V is the reaction vessel, in which spherical electrodes of nickel, about 5 mm in diameter, are inserted. The spark gap is kept at 2 mm. The sparking potential from 0 volt to 15000 volts is obtained continuously through transformers T_1 and T_2 , and measured by the microammeter μA with a high resistance R .

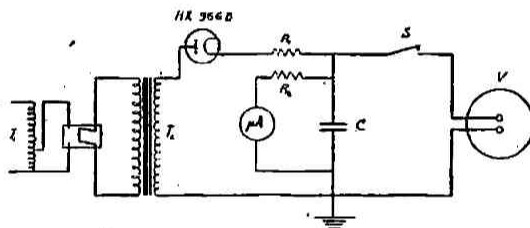


Fig. 5.

Oxygen and hydrogen contained in bombs were used by mixing in equal volumes. The explosion was detected by a mercury manometer connected with the reaction vessel, and at the same time the amount of reaction was measured.

Experimental Procedure and the Results.

1. Spark peninsula in the air.

In the first place, the relation between the pressure and the sparking potential in the air was sought. The potential was given to the electrodes by the following two methods:

(a) *Spark by statical voltage.* The switch S , in Fig. 5, being closed, voltage was continuously raised with an autotransformer and made to reach the sparking potential (V_s).

(b) *Spark by impulse voltage.* The switch S being opened, a given voltage (V_s) was read by the microammeter, μA , and then S was suddenly closed and the voltage was impulsively applied to the electrodes in the reaction vessel.

The emission of spark was detected by sound, luminescence, and deflection of the microammeter. At the first discharge made with the electrodes left to stand

for more than 1 hour, the sparking potential was remarkably high and irregular, but at the discharges made in succession every few minutes the sparking potentials were much lower and regular. In the experiments mentioned below, these regular sparking potentials were adopted. An instance is shown in Table I.

Table I.

Air pressure (mm)	1st impulsive sparking potential V_{01} (volt)	Sparking potentials after 2nd discharge	
		V_1 (volt)	V_2 (volt)
1	1020	460	760
18	1680	410	610
34	2000	510	820
103	3780	1020	1480

The fact that, when the electrodes left to stand for a long time were used, the sparking potential was unusually high, is considered to be caused by variation in the quality of the surface of the electrodes. This variation is probably due to contamination by the vapour of grease and other substances. The polishing of the surfaces of the electrodes can somewhat lessen this influence, but in the present experiments such polishing was not made. It is a well-known fact⁷⁾ that the sparking potential is strikingly affected by the surface of the electrodes, especially that of the cathode, and it is note-worthy as one of the fundamental characteristics of spark and spark ignition.

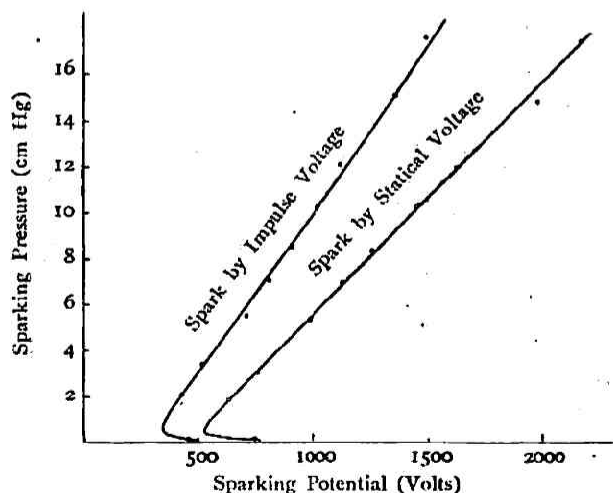


Fig. 6.

The air was exchanged at every discharge, for without the exchange the sparking potential was slightly low and irregular. The spark peninsula thus

7) Loeb, *Electrical Discharge*, p. 451.

obtained is shown in Fig. 6, which gives nothing but Paschen's Law. The result shows that at the same pressure V_i is generally larger than V_s , i.e., spark is brought forth more easily by the impulse voltage than by the statical voltage. Namely, it is clear that the sparking potential is dependent on the rate of change of the electrode potential. In the experiments mentioned below, spark was emitted by the statical voltage.

2. Spark ignition in oxyhydrogen gas.

Various potentials were statically applied to the electrodes in oxyhydrogen gas under various pressures and the conditions for the spark ignition or explosion were observed.

(a) *Detection of Spark Ignition.* Spark was detected by the methods mentioned above, and the explosion caused by the spark or spark ignition was detected by

- (i) luminescence covering the whole reaction vessel,
- (ii) jump of mercury head in the manometer, and
- (iii) decrease of the total pressure after discharge.

If an explosion occurs and the reaction makes a complete progress, the pressure decrease ΔP is generally proportional to the initial pressure, that is,

$$\Delta P = aP - b, \quad (1)$$

where a is a constant and b is the vapour pressure of the water vapour at room temperature. When the pressure of the water vapour generated is lower than that of the water vapour at room temperature, ΔP is expressed as follows:

$$\Delta P = cP, \quad (2)$$

where c is a constant. Both relations (1) and (2) are valid only when the reaction is complete. If an explosive reaction means a complete reaction these relations are considered to be the necessary conditions for an explosive reaction, and so they can be used for detection of an explosion with other characteristics. Equation (2), however, was not actually confirmed. This seems to mean that the reaction becomes incomplete at such low pressures.

(b) *Pressure decrease after spark discharge and pressure limits of explosion.* Figs. 7 to 12 show the relation between ΔP and P obtained at various sparking potentials with regard to oxyhydrogen gas ($H_2:O_2=1:1$). From these results it is seen that there exist three regions at least.

(i) Region of spark without explosion.—In this region, though spark is emitted, ΔP is negligibly small and not applicable to equation (1); the reaction is incomplete. When spark discharge is made to occur repeatedly in such a state,

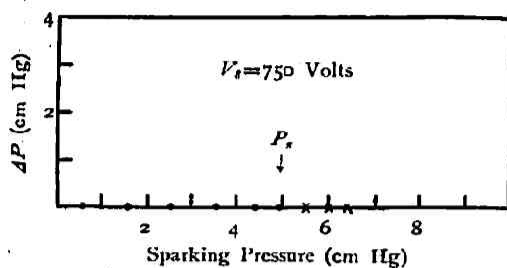


Fig. 7.

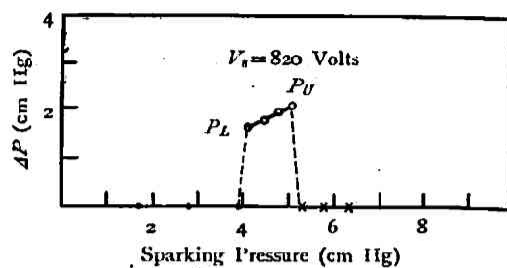


Fig. 8.

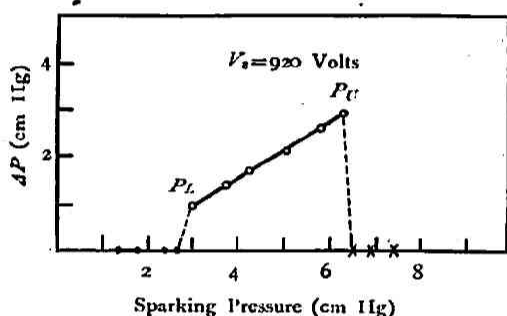


Fig. 9.

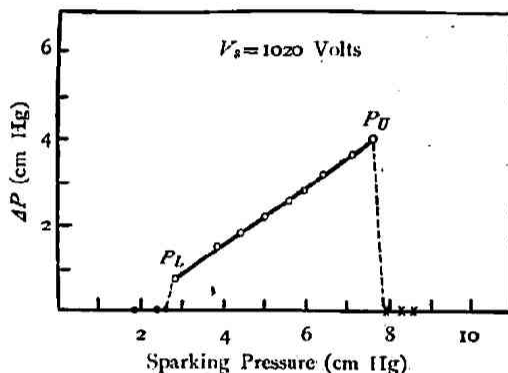


Fig. 10.

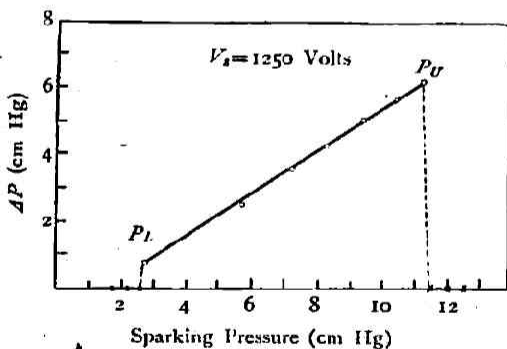


Fig. 11.

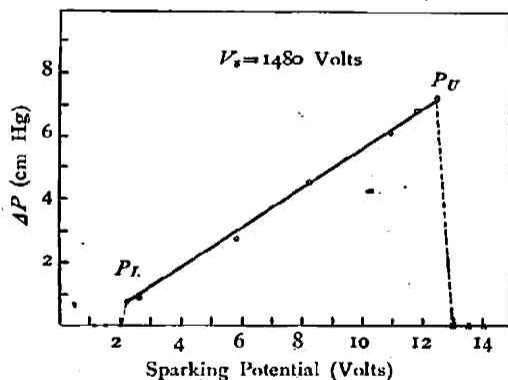


Fig. 12.

a stable arc of crimson red colour appears between the electrodes, which is not recognized at a higher pressure. This phenomenon will be discussed in another report.

If the initial pressure is lower than 1 mm, it is expected from Paschen's Law that there will appear no spark region. In the present experiment, however, no observation of it was tried.

(ii) Region of spark ignition.—In this region, explosion occurs simultaneously with spark, and ΔP generally increases in proportion to P . The reaction is com-

pleted between the two pressure limits,—upper limit (P_U) and lower limit (P_L). At the same time, luminescence covering the whole range and a pressure kick are recognized; this suggests an occurrence of explosion. Near the lower limit, however, explosion is so weak that the luminescence can be detected only in a dark room.

(iii) Non-spark region.—When pressure is higher than P_U , no spark can be emitted any longer at the said potential, and accordingly no reaction occurs. The case where spark discharge was made and yet no explosion occurred was not found at any pressure higher than P_U .

In Fig. 7, both the region of spark without explosion and non spark region are seen but not the region of spark ignition. In this case P_U is clearly the upper pressure limit of spark discharge.

(c) *Spark ignition peninsula.* Those results mentioned in the previous section are plotted in Fig. 13 with respect to the pressure and sparking potentials. Thus the $P-V_s$ field is divided into three regions:

- (i) Region of spark without explosion (under CBD).
- (ii) Region of spark ignition (within ABD).
- (iii) Non-spark region (above ABC).

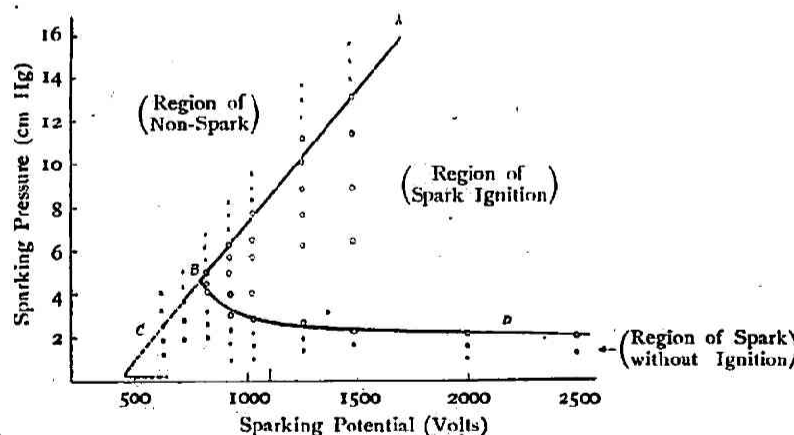


Fig. 13.

Region (ii) is nothing but the spark ignition peninsula to be sought after, though a little different from Fig. 4.

Discussion.

From the above experimental results the existence of the spark ignition peninsula with regard to oxyhydrogen gas ($H_2:O_2=1:1$) was confirmed. In other words, there are both the upper pressure limit and the lower limit of explosion for

a given sparking potential. This relation must be also valid if spark energy is substituted for sparking potential. In this respect, the spark ignition peninsula of Fig. 13 qualitatively agrees with the relation (Fig. 1) given by Lavrov. Lavrov, however, regarded the very upper limit merely as the limit of explosion and tried to support Semenov's chain theory, but it is clear from the said experimental results that at least in the case of oxyhydrogen the upper limit corresponds to the limit of sparking which is Paschen's Law itself. This is also clear from the fact that the upper limit curve can be extended to the region of spark without explosion. Whenever spark is emitted at a pressure higher than the lower limit, it is always accompanied by an explosion. This fact does not directly sustain Lavrov's idea that the activated molecules formed by spark is so deactivated at high pressure in the gaseous phase as to retard the chain reaction. It would be rather proper to consider that the upper limit of spark ignition agrees with the upper limit of sparking. According to the theory of spark discharge, the reason why spark is suppressed at a high pressure is that gaseous molecules existing in the spark gap becomes harder ionizable according as air pressure rises. On the other hand, it has been admitted that the sparking potential is remarkably influenced by the property of the surface of the cathode, and this suggests that sparking phenomena do not simply depend upon the conditions of the gaseous phase, though any definite conclusion has not yet been given. As a pre-condition for the emission of spark it is, at least, demanded that the gas becomes an electric conductor. It is also probable that the preliminary process before sparking has an important relation to chemical activation of gaseous molecules, and the most important field for that process is considered to be the surface of the cathode or its neighbourhood. In other words, it is not unreasonable to assume that spark discharge and explosion take the same primary process. Experiments on this subject are being continued under other conditions.

Summary.

- (1) Spark peninsula and spark ignition peninsula against thermal explosion peninsula have been defined and experimentally confirmed in the air and oxyhydrogen gas.
- (2) It is concluded that the upper limit in the case of spark ignition agrees with that of spark itself.
- (3) It is suggested that the primary process of spark and that of explosion are in a close relation.

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